

Multilevel ionic co-assembly of a terpyridyl complex and polyoxometalate: Dual outcomes from frameworks to close packings

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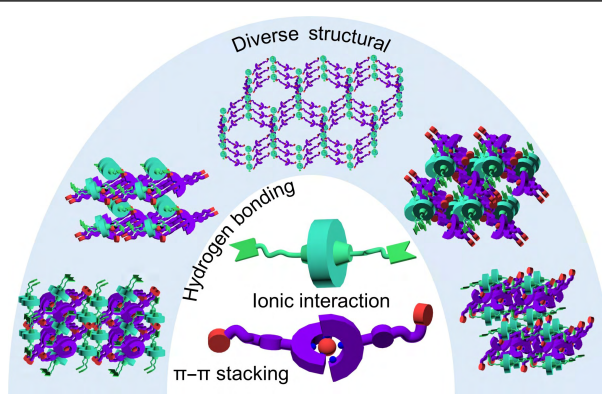


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ABSTRACT: The coexistence of multiple noncovalent interactions, such as ionic interactions, hydrogen bonding, and π - π stacking, provides rich opportunities for constructing supramolecular architectures while presenting challenges in controlling assembly outcomes. Herein, we employ hydrogen bond-functionalized Anderson-type polyoxometalates and terpyridyl-based metal complexes as complementary building blocks. By varying the solvent, temperature, and assembly time, we achieve distinct supramolecular structures. Rapid assembly in water yields a kinetically trapped two-dimensional hexagonal ionic framework. By contrast, assembly in *N,N*-dimethylformamide–water mixtures under ambient or hydrothermal conditions leads to four thermodynamically stable ionic crystals, each characterized by unique packing arrangements governed by π - π stacking and hydrogen-bonding interactions. This study demonstrates that a single co-assembly system can generate diverse, well-defined architectures under different assembly conditions, offering a practical strategy for the controlled construction of complex supramolecular materials.



KEYWORDS: polyoxometalates, terpyridyl complexes, noncovalent interactions, ionic crystal

The coexistence of multiple noncovalent interactions within a supramolecular system offers rich structural possibilities while posing challenges for precise regulation [1–4]. Polyoxometalates (POMs) feature well-defined sizes, geometries, and modifiable sites, making them ideal platforms for integrating multiple interaction types [5–8]. In particular, covalent functionalization of the Anderson-type MnMo_6 cluster with carboxyl-containing groups (HOOC-MnMo_6) introduces directional hydrogen-bonding capabilities, enhancing its utility for oriented assembly [9–15]. Meanwhile, bis(terpyridyl) metal complexes (M-TPY) represent another essential building unit; their octahedral geometry provides stability and directionality [16–18], enabling the formation of one-dimensional (1D) motifs via π - π stacking interactions [19–21]. Although the ionic co-assembly of POMs and large cations has yielded porous supramolecular frameworks [22–25], the potential for accessing broad architectural diversity governed by secondary

interactions remains underexplored. Herein, using the assembly of HOOC-MnMo_6 and M-TPY as a model system, we demonstrate that variations in solvent, temperature, and assembly time allow access to multiple structural states. Under rapid assembly conditions in pure aqueous solution, fast interionic association yields a two-dimensional (2D) hexagonal ionic framework (IF) with a $[2 + 3]$ hexagonal packing pattern. By contrast, introducing *N,N*-dimethylformamide (DMF) as a cosolvent and extending the assembly time at ambient temperature steer the system toward thermodynamic stability, resulting in three distinct ionic crystals (ICs): block-like (IC-block), needle-like (IC-needle), and plate-like (IC-plate) structures. A fourth needle-like phase (IC-HT) was obtained under hydrothermal conditions. The charge mismatch between HOOC-MnMo_6^{3-} and M-TPY^{4+} , coupled with the presence of additional ions (i.e., SO_4^{2-} and H^+), creates a complex charge-balance landscape that drives structural diversification. Specifically, sulfate anions participate in the assembly of the IC-block, yielding an overall stoichiometry of $\text{HOOC-MnMo}_6/\text{M-TPY}/\text{SO}_4 = 1:1:1$. Both the IC-needle and IC-plate exhibit a $\text{HOOC-MnMo}_6/\text{M-TPY}$ ratio of 3:2, whereas IC-HT adopts a 1:1 ratio. These distinct stoichiometries directly influenced the spatial organization of the components. In all crystalline forms, M-TPY units form 1D π - π stacked arrays with varying orientations: Both IC-block and IC-HT exhibit inclined stacking, IC-needle displays nearly flat-lying arrangements, and IC-plate adopts a standing-up mode. The POMs form diverse hydrogen-bonded networks and associate with the

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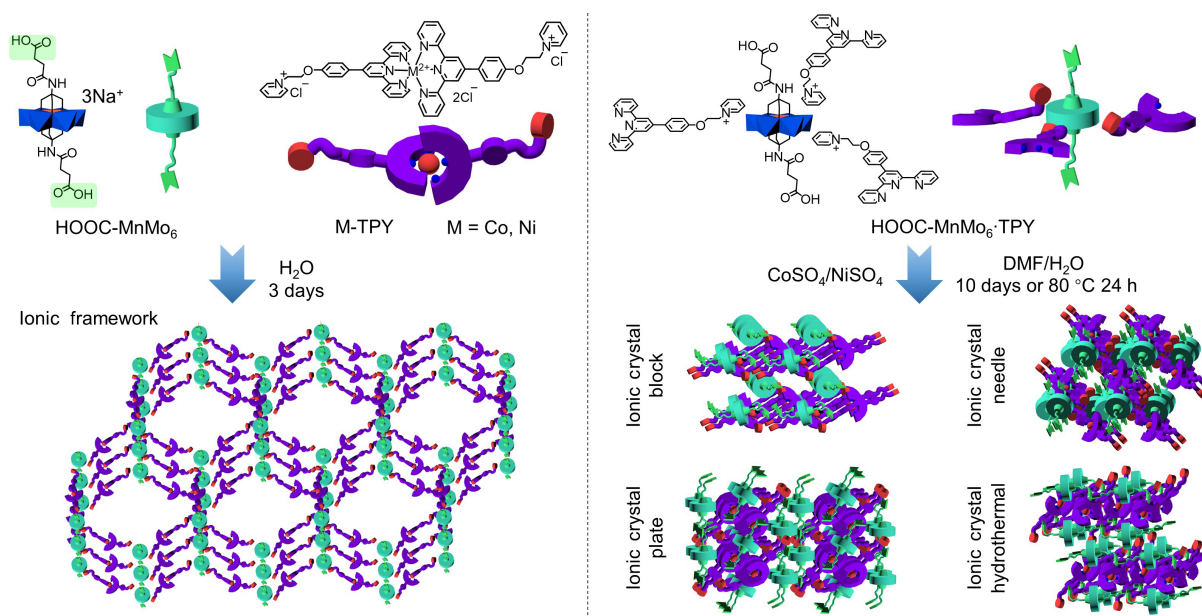
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cationic arrays via ionic interactions in either parallel or interpenetrating arrangements, ultimately leading to four distinct three-dimensional (3D) packing modes (Scheme 1). This system provides a clear example in which modulation of assembly conditions directs the synergistic interplay of secondary forces to generate a spectrum of ordered structures from identical components.

We first investigated the formation of a 2D hexagonal IF under rapid assembly conditions. The construction strategy for this system was based on the hierarchical control of multiple noncovalent interactions. Pre-coordination of metal ions (Co^{2+} or Ni^{2+}) with the terpyridine ligand formed octahedral metal-terpyridine complexes (Figs. S1–S3 in the Electronic Supplementary Material (ESM)). This configuration effectively shielded the metal ions from direct electrostatic attraction to the giant anions, thereby directing the POMs to selectively bind to the terminal pyridinium cations of the terpyridine units. This coordination was confirmed via X-ray photoelectron spectroscopy. The Ni $2p_{1/2}$ and $2p_{3/2}$ binding energies were observed at 873.44 and 855.82 eV, respectively, which were shifted from those of the NiSO_4 precursor (874.1 and 856.3 eV) [26]. Similarly, the Co $2p_{1/2}$ and $2p_{3/2}$ binding energies were found at 796.21 and 780.43 eV, respectively, compared with 804.7 and 788.5 eV for CoSO_4 [27] (Fig. S4 in the ESM). These shifts confirm the successful coordination of the metal ions (Co^{2+} and Ni^{2+}) to the terpyridine ligands. Ultraviolet–visible (UV–vis) spectra of the complexes showed characteristic metal-to-ligand charge transfer (MLCT) bands at 342 nm (Ni) and 372 nm (Co), which are distinct from those of the free ligand, further verifying the successful coordination (Fig. S5 in the ESM). HOOC-MnMo_6 ($\text{Na}_3\text{MnMo}_6\text{O}_{18}[(\text{OCH}_2)_3\text{CNCO}(\text{CH}_2)_2\text{COOH}]$) was synthesized according to previously reported methods [28]. Co-assembly was then conducted by mixing M-TPY and HOOC-MnMo_6 in water at a molar ratio of 3:2, with Cl^- serving as the counterions of M-TPY. This combination promptly yielded a flocculent precipitate, and

after standing for three days, stable sheet-like assemblies were obtained (Fig. 1(a)). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses showed that the assemblies were tens of micrometers in size with irregular edges (Fig. S6 in the ESM). Elemental analysis confirmed an M-TPY to HOOC-MnMo_6 molar ratio of 3:2, consistent with the designed stoichiometry (Tables S1 and S2 in the ESM). Based on this stoichiometric ratio, combined with the dimensional analysis of the individual building units, we constructed a structural model of a 2D hexagonal IF driven primarily by ionic interactions (Fig. S7 in the ESM). Using this model, we performed Pawley refinement against the experimental powder X-ray diffraction (PXRD) data (Figs. S8 and S9 in the ESM), which yielded fitted unit cell parameters of $a = 6.43$ nm and $c = 2.54$ nm for Ni-IF and $a = 6.21$ nm and $c = 2.40$ nm for Co-IF. These values are in reasonable agreement with the theoretically estimated dimensions ($a = 6.4$ nm and $c = 2.5$ nm) derived from molecular modeling [29]. However, the PXRD data alone do not provide definitive crystallographic proof for such a framework. To further substantiate the structural model, we performed high-resolution TEM (HRTEM) imaging and gas adsorption measurements. In the HRTEM images, the POM clusters containing heavy atoms exhibited pronounced dark contrast and were uniformly distributed throughout the assemblies. Owing to the electron-beam sensitivity of the sample and thermal drift, we were unable to obtain an ordered hexagonal lattice. Instead, only some clusters were observed to arrange into distorted hexagonal patterns, with edge lengths consistent with those of the proposed framework model (Fig. S10 in the ESM). However, gas adsorption measurements using N_2 and CO_2 indicate a pore size of approximately 2.1 nm, which agrees well with the proposed structural model of the ionic framework (Fig. S11 in the ESM). Additionally, Fourier transform infrared (FTIR) spectra showed that the redshift, broadening, and decreased intensity of the carbonyl ($\text{C}=\text{O}$) stretching vibration peak provided evidence for the



Scheme 1 Schematic illustration of the controlled co-assembly pathways. Left: The rapid combination of HOOC-MnMo_6 and M-TPY ($M = \text{Co}, \text{Ni}$) building blocks in pure water leads to the kinetic trapping of a 2D hexagonal ionic framework with a [2+3] packing pattern. Right: Employing the pre-formed electrostatic complex $\text{HOOC-MnMo}_6\text{-TPY}$ as a starting material, subsequent coordination with metal ions in a DMF/ H_2O mixed solvent directs the assembly toward thermodynamic minima. This yields four distinct ionic crystals—IC-block, IC-needle, and IC-plate at ambient temperature over 10 days, and IC-HT under hydrothermal conditions. This scheme underscores how the assembly pathway and conditions dictate the structural divergence from a single system.

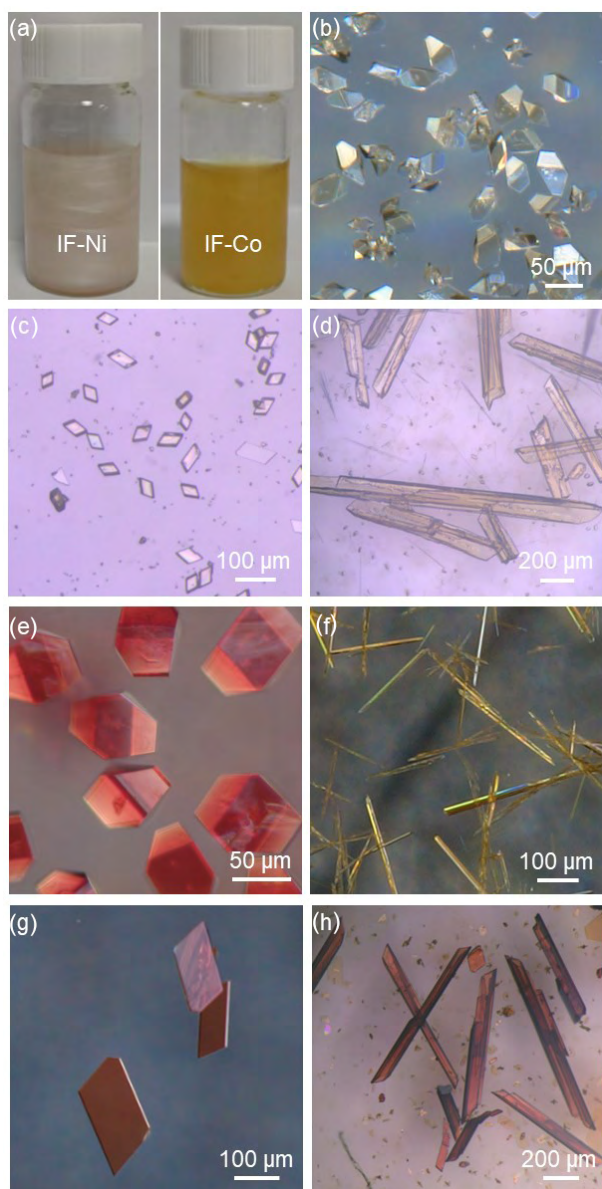


Figure 1 (a) Photographs of the aqueous dispersions of the ionic frameworks (IF-Ni and IF-Co). (b)–(h) Optical micrographs of the single crystals: (b) Ni-block, (c) Ni-plate, (d) Ni-HT, (e) Co-block, (f) Co-needle, (g) Co-plate, and (h) Co-HT.

formation of hydrogen bonds, confirming their crucial role in the 3D ordered structure (Fig. S12 in the ESM) [30]. Collectively, these complementary techniques consistently support the hexagonal framework as the most reasonable structural interpretation of the rapid aqueous assembly.

To further evaluate the generality of hexagonal framework formation, we extended the assembly of Ni-TPY with HOOC-MnMo_6 to mixed-solvent systems comprising H_2O and methanol, acetonitrile, or acetone while keeping all other conditions identical to those used for IF formation in pure water. SEM imaging revealed distinct morphological transformations depending on the solvent composition: Sheet-like morphologies were gradually replaced by ribbons, rods, or fibers as the organic solvent content increased, reflecting solvent-modulated assembly kinetics and intermolecular interactions (Figs. S13–S15 in the ESM). Despite these morphological variations, elemental analysis confirmed that the Ni-

TPY to HOOC-MnMo_6 molar ratio remained $\sim 1.5:1$ across all tested solvent systems (Tables S3–S5 in the ESM), consistent with the IF stoichiometry. PXRD analysis further showed that the assemblies obtained in $\text{H}_2\text{O}/\text{CH}_3\text{OH}$, $\text{H}_2\text{O}/\text{CH}_3\text{CN}$, and $\text{H}_2\text{O}/\text{acetone}$ could all be indexed to a hexagonal lattice, with fitted unit cell parameters comparable to those of the IF obtained in pure water (Figs. S16–S18 in the ESM). These results demonstrate that, although the hexagonal framework architecture is largely preserved over a range of solvent conditions, the assembly morphology can be tuned by varying solvent composition.

Building on the successful construction of the hexagonal IF, we next explored the structural diversity accessible within this co-assembly system. In contrast to the previous strategy, the current approach began with the electrostatic association of POMs and terpyridine cations to form the ionic composite $\text{HOOC-MnMo}_6\cdot\text{TPY}$, followed by the introduction of $\text{Co}^{2+}/\text{Ni}^{2+}$ to drive self-assembly. Specifically, $\text{HOOC-MnMo}_6\cdot\text{TPY}$ and CoSO_4 or NiSO_4 were separately dissolved in a $\text{DMF-H}_2\text{O}$ (1:1, v/v) mixture and then combined at a molar ratio of 2:3. Immediately after mixing, a flocculent precipitate formed but gradually dissolved over time. After ten days, crystals with three distinct crystal habits—block, needle, and plate—were simultaneously obtained. The Co system yielded all three crystal types, while the Ni system produced only block- and plate-shaped crystals. Additionally, heating the reaction mixture under hydrothermal conditions at 80°C for 24 h yielded a distinct IC-HT (Figs. 1(b)–1(h)). High-quality single crystals of each morphology were selected for single-crystal X-ray diffraction analysis. All seven crystals crystallize in the triclinic space group $P\bar{1}$ (Tables S6–S12 in the ESM), and the identity of the central metal ion has no significant influence on the crystal habit and architecture. Therefore, the seven single-crystal structures are categorized into four structural types. In the IC-block structure, M-TPY and HOOC-MnMo_6 assemble in a 1:1 stoichiometric ratio, with SO_4^{2-} serving as a counterion, giving a charge ratio of 4:5 (Figs. S19 and S20 in the ESM). Considering the acidic conditions (pH 3–4), the remaining uncompensated positive charge is presumed to be balanced by H^+ . At the supramolecular level, M-TPY units form 1D linear arrays through π – π stacking and $\text{C-H}\cdots\pi$ interactions, with the M-TPY molecules inclined at an angle of 35.25° relative to the array direction. Within these arrays, the pyridine ring of the terpyridine unit engages in continuous π – π stacking with the benzene ring and pyridinium ring of adjacent M-TPY molecules, while multiple $\text{C-H}\cdots\pi$ interactions involving methylene groups, pyridine rings, and pyridinium head groups further stabilize the 1D architecture (Tables S13 and S14 in the ESM). Simultaneously, SO_4^{2-} bridges the amide and carboxyl groups on the POM side chains via hydrogen bonds, forming 1D anionic arrays (Tables S15 and S16 in the ESM). The cationic π – π -stacked arrays and anionic hydrogen-bonded arrays are interconnected through ionic interactions, giving rise to the characteristic 3D packing of the IC-block (Fig. 2(a); Tables S17 and S18 in the ESM). When viewed along the b axis, the structure contains voids that are occupied by DMF molecules (Fig. S21 in the ESM).

In the IC-needle, M-TPY and HOOC-MnMo_6 assemble in a 2:3 stoichiometric ratio, corresponding to a charge ratio of 8:9 (Fig. S22 in the ESM), with the remaining positive charges likely compensated by H^+ under acidic conditions. M-TPY units form 1D linear arrays through π – π stacking and $\text{C-H}\cdots\pi$ interactions, with molecular planes inclined at a small angle of 12.69° relative to the array direction, resulting in a nearly flat-lying arrangement. This

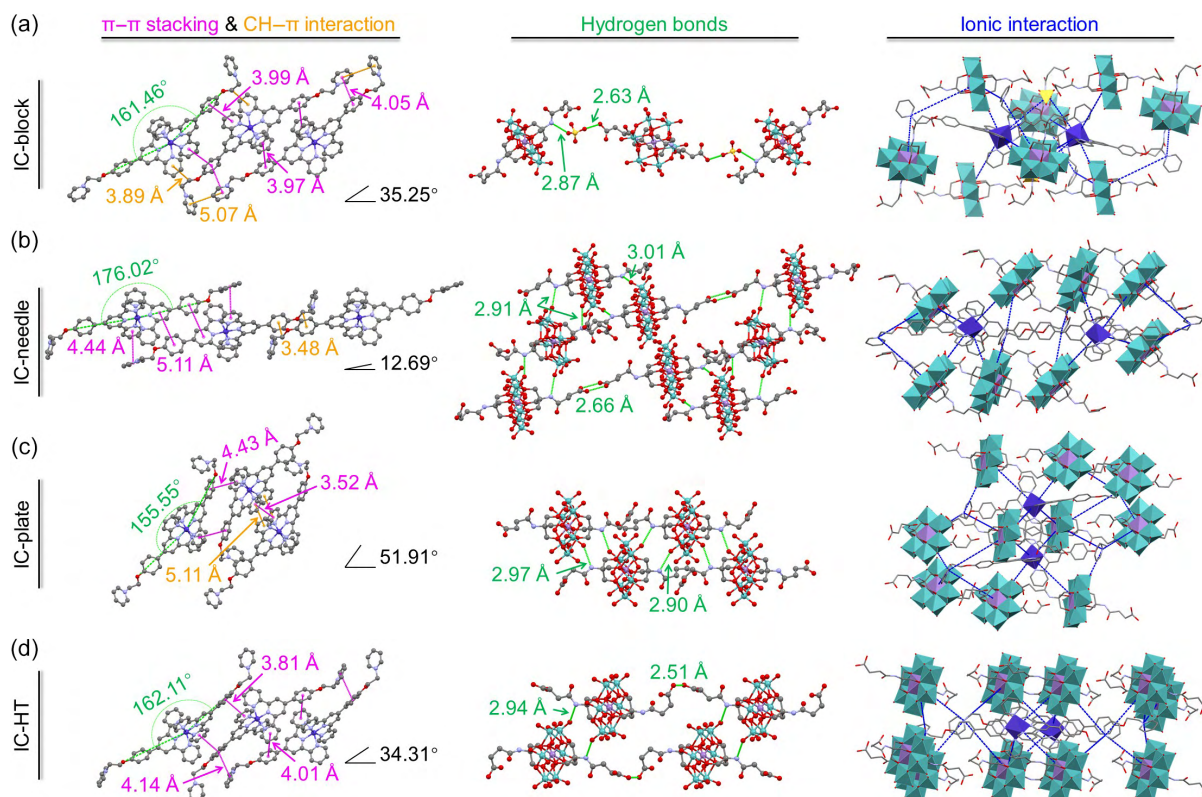


Figure 2 Structural models depicting the hierarchical interplay of noncovalent forces in (a) IC-block, (b) IC-needle, (c) IC-plate, and (d) IC-HT (shown with Co as a representative example; the Ni analogues adopt essentially identical packing arrangements). The specific combinations of π - π stacking, C-H- π interactions, hydrogen bonds, and ionic interactions direct the unique assembly of each architecture.

low-angle packing increases the intermolecular offset, giving rise to an additional π - π interaction between the pyridinium cation and a pyridine ring of an adjacent terpyridine group (Table S19 in the ESM). Notably, although SO_4^{2-} was present during crystallization, it was not incorporated into the final assembly. Instead, pairs of carboxyl groups are linked through dual hydrogen bonds, while additional hydrogen bonds between the amide groups and terminal oxygen atoms of the POMs construct a 2D anionic hydrogen-bonded network (Table S20 in the ESM). This hydrogen-bonded network interweaves with the 1D cationic π - π -stacked arrays, collectively giving rise to the characteristic 3D packing of the IC-needle (Fig. 2(b); Table S21 in the ESM). When viewed along the c axis, elliptical nanochannels are observed and are partially occupied by DMF molecules (Fig. S23 in the ESM).

In the IC-plate structure, M-TPY and HOOC-MnMo_6 also adopt a 2:3 stoichiometric ratio, with the remaining positive charges compensated by H^+ (Figs. S24 and S25 in the ESM). Its defining structural feature is a standing-up packing mode, in which the molecular plane of the M-TPY is inclined at an angle of 51.91° relative to the array direction, with alternating offset stacking along the propagation direction of the 1D π - π stacked columns (Tables S22 and S23 in the ESM). Meanwhile, adjacent HOOC-MnMo_6 units are interconnected through dual hydrogen bonds between side-chain amide groups and terminal oxygen atoms, thereby constructing a 1D anionic array (Tables S24 and S25 in the ESM). Remarkably, the cationic π - π -stacked arrays and the anionic hydrogen-bonded arrays are aligned parallel to one another through electrostatic interactions, forming a compact layered architecture (Fig. 2(c); Tables S26 and S27 in the ESM).

In addition to obtaining thermodynamically stable crystals

through prolonged assembly in DMF/ H_2O , we employed a hydrothermal method to significantly reduce the assembly time. Needle-like IC-HT crystals were obtained after just 24 h under autogenous pressure at 80 °C. This structure exhibits distinct characteristics: M-TPY and HOOC-MnMo_6 assemble in a 1:1 stoichiometric ratio without the incorporation of SO_4^{2-} , corresponding to a charge ratio of 4:3 (Figs. S26 and S27 in the ESM). We propose that the missing negative charge is compensated by deprotonation of the carboxyl groups on the HOOC-MnMo_6 side chains, with the released H^+ remaining in the surrounding environment. To verify this hypothesis, Co-HT was characterized via FTIR spectroscopy and compared with the HOOC-MnMo_6 -TPY ionic composite precursor. The FTIR spectrum shows a redshift of the -COOH stretching vibration from 1729 to 1716 cm^{-1} , confirming the formation of hydrogen bonding. Meanwhile, the appearance of peaks at 1619 and 1369 cm^{-1} , attributable to the asymmetrical and symmetrical stretching vibrations of $-\text{COO}^-$, respectively, indicates the presence of deprotonated carboxylate groups (Fig. S28 in the ESM). The coexistence of -COOH and $-\text{COO}^-$ groups in the crystal strongly supports the proposed charge-compensation mechanism.

Structurally, the terpyridine complexes adopt inclined 1D π - π -stacked arrays similar to those in IC-block (Tables S28 and S29 in the ESM). Adjacent HOOC-MnMo_6 units connect via single hydrogen bonds between -COOH and $-\text{COO}^-$ groups—a motif distinct from the dual hydrogen bonds between carboxyl groups in IC-needles—and via hydrogen bonds between the amide groups and terminal oxygen atoms of the POMs, cooperatively forming a unique double-chain 1D architecture (Tables S30 and S31 in the ESM). The cationic π - π -stacked arrays and the anionic HOOC-

MnMo₆ double-chain arrays are aligned parallel to one another through electrostatic interactions (Fig. 2(d); Tables S32 and S33 in the ESM), forming nanochannels along the *c*-axis that are partially occupied by DMF molecules (Fig. S29 in the ESM).

To gain a comprehensive understanding of the bulk-phase assemblies beyond the single-crystal structures, we performed a series of complementary characterizations on the as-prepared crystalline materials. NMR spectroscopy was conducted in DMSO-*d*₆, a strongly polar solvent capable of dissolving these ionic assemblies. Upon dissolution, the ionic interactions and hydrogen bonding are inevitably weakened or disrupted. Compared with the free assembly components, the proton signals of the M-TPY cations in the dissolved frameworks showed distinct splitting and downfield shifts (Fig. S30 in the ESM), confirming the successful replacement of the original Cl[−] counterions by the anionic HOOC-MnMo₆ clusters during assembly formation. To evaluate the phase composition of the bulk products, PXRD patterns were collected and compared with simulated patterns derived from single-crystal structures (Figs. S31(a) and S31(b) in the ESM). For the ICs obtained under ambient conditions, the experimental PXRD patterns exhibited multiple sets of diffraction peaks, confirming the coexistence of different crystalline phases. Quantitative analysis based on elemental composition (Tables S34 and S35 in the ESM) yielded M-TPY/ HOOC-MnMo₆ molar ratios of 1:1.2 for the Co system and 1:1.4 for the Ni system. These values indicate that, in the Co system, IC-block accounts for ~ 60% of the bulk product, while IC-needle and IC-plate together comprise the remaining 40%; in the Ni system, IC-block accounts for ~ 20% of the bulk product, whereas IC-plate is the dominant phase, comprising ~ 80%. By contrast, for the hydrothermally obtained IC-HT, the experimental PXRD pattern agreed well with the simulated pattern calculated from its single-crystal structure (Figs. S31(c) and S31(d) in the ESM), indicating a relatively pure phase compared with the mixed-phase products obtained under ambient conditions. Elemental analysis confirmed an M-TPY/ HOOC-MnMo₆ ratio of 1:1, consistent with the proposed charge-compensation model involving deprotonated carboxylate groups (Tables S36 and S37 in the ESM).

The thermal stability and porosity of the assemblies were assessed via thermogravimetric analysis (TGA) and gas adsorption measurements. The TGA curves revealed three distinct weight-loss stages (Fig. S32 in the ESM). The first stage, below 240 °C, corresponds to the removal of DMF and water molecules; the

second stage involves the decomposition of the aliphatic segments, carboxylate groups, and ether linkages; and the third stage is attributable to the degradation of the thermally robust terpyridine aromatic rings. The frameworks remain stable up to ~ 240 °C, confirming their thermal robustness. Gas adsorption measurements using N₂ and CO₂ were performed on the activated materials. Notably, CO₂ exhibited significantly better uptake than N₂ in the low-pressure region and displayed a Type I adsorption isotherm characteristic. This difference is likely attributable to the charged and polar nature of the channels, which results in quadrupolar interactions with CO₂ rather than with N₂ molecules, thereby hindering their adsorption [31]. In addition, the large quadrupole moment of CO₂ enhances its affinity for the polar pore surfaces. Using CO₂ as the probe molecule, the pore size distribution was estimated to range from 0.35 to 0.82 nm (Fig. S33 in the ESM), consistent with the channel dimensions observed in the crystal structures.

To elucidate the dynamic process underlying the formation of these complex architectures, we monitored the assembly pathway. SEM images revealed that the assemblies initially existed as amorphous aggregates, which gradually aggregated and evolved into well-defined crystals with distinct habits. UV-vis absorption spectroscopy provided molecular-level insights into this process. The immediate emergence of the MLCT band at 342 nm upon initiation of assembly confirmed the rapid coordination between Ni²⁺ and terpyridine ligands, signifying a fast nucleation event. The constant peak position throughout the subsequent assembly process indicates the stability of the metal coordination centers, while the concurrent decrease in absorbance demonstrates the progressive growth of the aggregates (Fig. 3). Collectively, these findings demonstrate that the crystal formation proceeds through a distinct “nucleation–aggregation” growth mechanism.

The rich structural diversity observed in this system arises from several interconnected factors. First, the delocalized nature of the charges on the POM clusters renders the ionic interactions largely non-directional and unsaturated, allowing for flexible packing arrangements. Second, the inherent charge mismatch between the building blocks—specifically, the 4:3 charge ratio of M-TPY to HOOC-MnMo₆—necessitates the incorporation of additional counterions (such as SO₄^{2−} or H⁺) from the surrounding environment to achieve overall charge compensation. This adaptive charge-compensation mechanism gives rise to distinct stoichiometric ratios across the different crystalline products. Third,

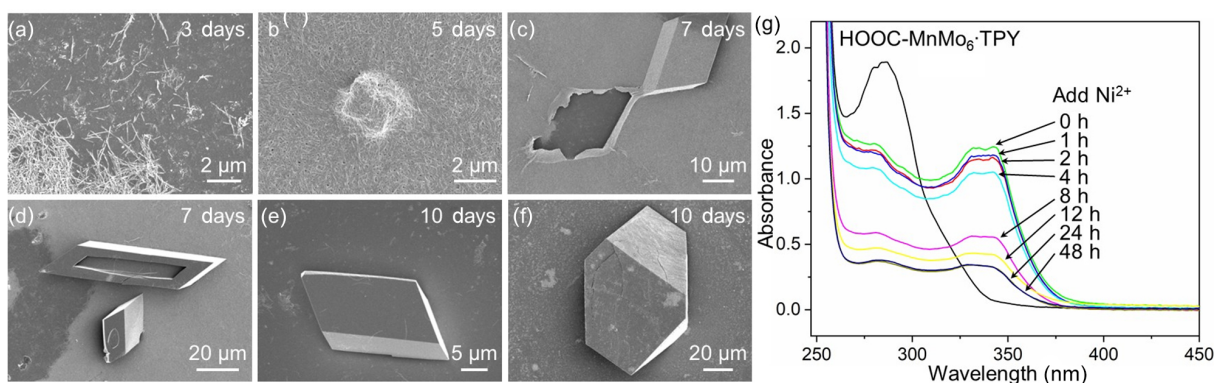


Figure 3 Time-dependent monitoring of the assembly process from an amorphous precipitate to defined crystals. (a)–(f) SEM images of the assemblies formed from HOOC-MnMo₆-TPY and NiSO₄ in a DMF/H₂O mixed solvent after (a) 3 days, (b) 5 days, (c) and (d) 7 days, and (e) and (f) 10 days, revealing the morphological evolution. (g) Time-evolution of the UV-vis absorption spectra (focusing on the MLCT band) for the co-assembly, showing rapid nucleation (immediate peak emergence at 342 nm) followed by aggregate growth (subsequent intensity decreases).

the metal–terpyridine coordination geometry exhibits remarkable conformational flexibility. The angles between the two terpyridine ligands coordinated to the same metal center vary across the four crystal structures, ranging from 155.55° to 176.02°, independent of the central metal identity. This conformational variation directly modulates the overall shape of the cationic building blocks, which in turn influences the 1D π – π stacking interactions. Consequently, the orientation of the M-TPY units relative to the 1D π – π stacking direction varies significantly among the four structures, with the angle between the molecular plane and the stacking axis ranging from 51.91° to 12.69°. This intrinsic flexibility allows the M-TPY units to adopt different conformations and packing orientations in response to different assembly environments, rather than being rigidly constrained to a single geometry.

In summary, we demonstrate that, in a complex supramolecular system containing multivalent components and competing interactions, structural outcomes are not limited to a single arrangement but can be strategically diversified. Using carboxyl-functionalized POMs and metal–terpyridine complexes, we show that simple variations in solvent, temperature, and time direct the system toward either a kinetically controlled 2D hexagonal ionic framework or a set of thermodynamic ICs with distinct packing modes. This study provides a clear and practical strategy for generating multiple well-defined architectures from a single co-assembly system by strategically regulating the interplay between charge compensation and hierarchical noncovalent forces.

Electronic Supplementary Material: Supplementary material (including synthetic procedures and characterization of M-TPY; preparation of IF and IC; SEM, TEM, EA, PXRD, FT-IR of IF; crystallographic parameters, structural diagrams, and FT-IR of IC; and CCDC Nos. 2504939 (Ni-block), 2504942 (Co-block), 2504941 (Co-needle), 2504940 (Ni-plate), 2504943 (Co-plate), 2504944 (Ni-HT), and 2504945 (Co-HT)) is available in the online version of this article at <https://doi.org/10.26599/POM.2026.9140151>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.”

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work. Author Lixin Wu is the advisory board member of this journal, but he is not involved in the peer-review or decision of this article.

Author contribution statement

J. X. W. solved and refined the single-crystal structures, and wrote the manuscript; L. W. designed and conducted the experiments; M. F. W. provided useful discussions and suggestions for experiments;

L. C. K. collected and reduced the single-crystal diffraction data at the Shanghai Synchrotron Radiation Facility (SSRF); B. L. and L. X. W. directed the project and revised the manuscript.

Use of AI statement

None.

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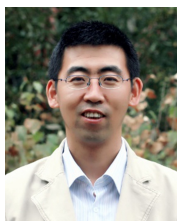
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